

AQUIFER RESTORATION TECHNIQUES

by

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The management and containment of waste and industrial by-products has resulted in increased application of geotechnology and other methods of aquifer protection and restoration. This paper will highlight a few of the methods currently in widespread use and will summarize the results of a National Water Well Association survey to determine current applications of technology in the industry today. The restoration techniques discussed will include pumping, treatment and recharge, slurry trench cutoff walls, grout curtains, biological and chemical treatment and activated carbon adsorption.

In determining the best method of pollution control or abatement, it is first necessary to form a conceptual model of the site. Site specific studies should be conducted to determine the geological environment, depth and quantitative aspects of groundwater flow, and extent of contaminated plume. These studies should include geologic mapping, air photography, collection of water well logs, test borings and field testings such as aquifer slug tests and drawdown rates. Seismic and magnetic surveys can help pinpoint geologic anomalies such as faulted areas and dikes. Geophysical electrical methods such as the self-potential method help in delimiting plumes of contaminants which are strongly concentrated, near the surface, and of strongly contrasting ionic strength as compared with native groundwater. Measurement of resistivity (the reciprocal of conductivity) can be very helpful in detecting and delimiting sand and gravel deposits. It is known for instance that unsaturated lithologic units have higher resistivity than saturated units, that saturated clays have low resistivities, that geologic units saturated with high ionic strength solution will have low resistivities whereas those saturated with solutions of low ionic strength will probably have high resistivities. In general, rocks except metal ores and clay minerals are insulators and

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thus have high resistivities. Gamma ray logs delineate shale or nonporous beds. Neutron logs measure indirectly the hydrogen content of a formation because hydrogen slows neutrons. Where the formation contains little clay, shale or hydrogen in chemical combination with solids, neutron logs can be calibrated to measure average porosity. Seismic refraction methods can be used for finding the thickness of unconsolidated material overlying bedrock. Aquifer information should include direction of flow, transmissivity, storativity and other relevant parameters.

After data has been collected, the objective of the remedial action should be determined. It may vary from complete containment of waste source and decontamination of the plume to containment of the source while allowing the contamination of the plume to simply disperse with time. In all clean-up operations, some sort of monitoring system should be installed, first to identify problem areas and secondly to monitor results of the actions undertaken.

Economics often restrain the number of monitoring wells an operator is willing to drill. Keely (1982) has outlined a chemical time sampling methodology which can increase the precision of data obtained from a small number of wells. Samples pumped and measured as a function of time represent groundwater from successively further points away from the well. Static water levels of each well are measured prior to the onset of pumping. The aquifer itself must be kept in a steady-state configuration. A pump in one of the wells is started and water level measurements are taken at logarithmically spaced intervals. At the same time, chemical samples and drawdown readings are taken in nearby non-pumping wells. After several hours, a second pumping well is started so that two wells are running continuously. According to Keely's research, "the two wells will compete for waters within their mutually overlapping cones of depression. The artificial groundwater divide, separating waters withdrawn into each well, will potentially result in isolation of the contaminant(s)

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on one side of the divide." The relationship between the total volume of water pumped to the distance the water traveled can be correlated given the effective aquifer porosity and aquifer thickness. Volume of water taken is divided by the effective porosity to determine aquifer volume. If the thickness of the aquifer can be approximated, the formula $V = \pi r^2 h$ permits the calculation of the distance the water traveled at the time of measurement. Each monitoring well will yield estimates specifically influenced by aquifer characteristics in that particular locality.

Once the quantitative and qualitative aspects of the contamination have been determined remedial actions are initiated. One method of waste containment involves the excavation of a trench through or under a slurry of bentonite clay and water to an impermeable layer. The trench is then backfilled with the original soil or with a soil and slurry mixture. If soil is mixed with slurry, the composition should stand a 10:1 slope with a water content around 35%. The minimum amount of bentonite for this composition ranges in most cases from about 0.5% to 2%. Lowest permeabilities are obtained with fine-grained sediments (particles passing a 200 mesh sieve) and may or may not be obtained from the excavation itself. The slurry is generally 4 to 7% by weight suspension of bentonite in water. It acts to prevent cave-ins and slumping and also forces bentonite into the soil on trench walls and bottoms. A filter cake, a layer of soil and bentonite exhibiting very low permeability, is formed on the trench sides. Once the trench has been excavated, backfilling is begun.

Tests conducted by the EPA to determine the ability of bentonite slurry walls to withstand the effects of various pollutants were very successful with the exception of alcohol. The following table lists the kinds of pollutants and their concentrations as tested by the EPA:

<u>Pollutant</u>	<u>Slurry bentonite backfill-30 to 40% fines</u>
Ca or Mg @1,000 PPM	N
Ca or Mg @10,000 PPM	M
NH ₄ NO ₃ @10,000 PPM	M
HCl	M
H ₂ SO ₄	N
HCl	H
NaOH (1%)	M
CaOH (1%)	M
NaOH (5%)	H
Sea Water	M
Acid Mine Drainage FeSO ₄ (pH 3)	N
Lignin (in Ca solution)	N

EPA 625/6-82-006

N - No significant effect

M - Moderate effect - permeability increase by factor of 2 to 5

H - Significant dissolution likely - permeability increase by a factor of 5 to 10

The NWWA Aquifer Restoration Techniques survey showed that additional contaminants have been contained effectively by slurry walls. These include Cr, Cr⁺⁶, As, Na, Mg, Cd, chlorides, sulfates, dissolved solids, chemical oxygen demand (COD), total organic carbon (TOC), gasoline, and coal tar constituents. Compatibility testing using the actual site leachate is essential in determining the slurry wall composition since many kinds of organic and inorganic molecules can weaken the repulsive forces between hydrated clay particles resulting in flocculation and slurry wall collapse. The aluminum and silica fractions of bentonite are readily dissolved by strong acids and bases. The following table is a compilation of the information operators gave NWWA on the types of bentonite used with particular kinds of pollutants:

<u>Pollutants</u>	<u>Type of Bentonite</u>
1. Cr, Cr ⁺⁶	1.) Volcay SL-70 (tested by manufacturer and found compatible with waste chemicals)
2.) Volatile organics	2.) Bentonite/native sand

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| 3.) Chloride, sulfate, alkalinity, Na, Mg, Ca, dissolved solids, Fe, COD, TOC | 3.) 1-3% bentonite with 40% natural fines (particles finer than 200 mesh sieve) |
| 4.) Free products, gasoline, #2 diesel, benzene, xylene, toluene, halogenated organics and municipal landfill leachate | 4.) Sodium bentonite/natural soil |
| 5.) Sodium sulfate brine | 5.) Premium grade bentonite (Envirogel) |
| 6.) SO ₄ , Cu, Cd, Fe, low pH | 6.) No additives used in natural soil |
| 7.) Organics, dissolved solids and various salts | 7.) American Colloid Saline Seal 100-polymerized bentonite resistant to leachate attack |
| 8.) Landfill leachate, high conductivity, hardness, chlorides, iron | 8.) Saline Seal 100 |
| 9.) Coal tar constituents such as cyanide and phenols | 9.) Cement/bentonite |

Grout curtains are nearly three times as expensive as slurry walls and have their greatest applicability in sealing voids in porous or fractured rock. Grout pipes are drilled into the ground and then a chemical or cement grout is injected. Once an initial perimeter is thus completed, a secondary series of holes is installed midway between the first holes. This procedure is continued until essentially no grout is being taken in. Grout curtains injected up gradient of a waste site can divert groundwater flow around the contaminated area.

The grout material used can take a wide variety of forms and can be designed to set within wide limits of from 10 hours to a few seconds depending on the velocity of groundwater flow and required action. Portland cement with additives such as clay, sands, fly-ash and chemical grouts is the most widely used grout because of the

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relatively low cost of materials. Bentonite mixed with water at a rate of 5-25% by dry weight forms a gel and although it imparts little structural strength, it is an extremely effective water barrier in medium to fine textured sands with permeabilities around 10^{-3} or 10^{-4} cm/sec.

There were two surveys completed on grout curtains. Grout curtains were chosen for a tailings impoundment because the depth to the aquifer was too great to trench. A grout curtain to contain Cu, Mg, and Fe was injected at a depth of around 200 feet downgradient of the tailings impoundment. The grout barrier was a fractured granitic substrate and grout gel was pumped to attempt to seal fractures. Ten holes 20 feet apart were necessary for the grout curtain emplacement. The grout curtain itself measured 40 feet by 200 feet and took two and a half days to construct. Its projected length of service is 25 years. It has not yet been evaluated as to effectiveness, but once milling operations are reinitiated, the water levels in the impoundment will be checked and a chemical analysis done of waters downgradient. A pump back system was installed as a remedial action used in conjunction with the grout curtain.

Another survey was completed on a hazardous waste site. A grout curtain was placed downgradient of the site where a narrows occurred and was keyed into underlying granites and metamorphic rocks. One hundred and fifty grout holes with depths to 100 feet were emplaced; spacing varied from three to six feet due to fractures encountered in underlying bedrock. Where fractures were encountered, a clay core barrier was placed about the grout curtain. Configuration of the grout curtain was determined by prior drilling and coring and by water tests. The grout was a silica grout composed of muriatic acid and sodium silicate which tends to resist low pH water and which is not hazardous if dissolved. The hydraulic conductivity of the final emplaced barrier was tested and found to be

2.2×10^{-8} cm/sec.

Passive components (i.e. slurry trench cutoff walls and grout curtains) may be used alone or in conjunction with different kinds of treatment methods. Activated carbon is used to control organic contaminants such as TCE and PCE as well as certain heavy metals in groundwater. Nonpolar organic compounds are removed by activated carbon by adsorption resulting from chemical attractive forces. Polar organic compounds such as alcohols and ketones may not be very effectively removed because of their molecular electrical charges. Activated carbon is most effective if water is of relatively good quality (about 2.0 mg/l or less of TOC). In poorer quality waters, lower molecular weight organics can be desorbed by preferential adsorption of higher molecular weight compounds. The volatile chemical compounds observed to be amenable to treatment by activated carbon in a 1982 study by Enos L. Stoves (GWMR 1982) were all low molecular weight compounds of from 100 to 140 ams. Disadvantages of the system include the fact that the life of the bed may be very short in the presence of complex organic compounds such as humic acid and fatty acids prevalent in municipal landfill leachate. Also, cost of material, competitive adsorption and problems of removal and disposal of spent organic carbon may be prohibitive. In the NWWA survey, most of the contaminated water was pretreated prior to activated carbon adsorption. Pretreatment included physical chemical treatment such as filtering with sand to remove turbidity, cellulose fiber filtration, aeration to remove iron, other metals and more volatile organics, and oil/water separation. The following table gives a general cost breakdown where the information was obtainable from the NWWA survey.

<u>Pollutants</u>	<u>Gallons of water per pound of carbon used</u>	<u>Ave cost/lb of C fill</u>	<u>Cost per gallon</u>
Chlorinated & non- chlorinated organics 10-15 ppm	150-200 gal/lb	\$1.50-\$2.00	\$0.02

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TCE, dichlorethylene, alcohols, acetone 50-500 ug/l	11gal/lb	\$0.78/lb	\$0.25
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About half of the questionnaires indicated that the carbon would be disposed of while the other half indicated regeneration would be done offsite. In all cases, the treatment was regarded as very successful.

Biological treatment is another alternative in dealing with contaminated waters. Biologic techniques include activated sludge, aeration lagoons, composting and trickle filters. The actual components used will vary widely and depend on the amounts and kinds of contaminants dealt with. The bacteria known to be adapted to the breakdown of petroleum products include *Pseudomonas*, *Nocardia*, *Arthrobacter*, *Flavobacterium* and *Corynebacterium*. All of these organisms are aerobic and thus require proper aeration. Specialized strains have been developed for other specific chemicals. In all cases, biologic treatment is a slow and therefore economically less attractive treatment scheme.

Only one questionnaire was completed on biological in situ treatment. The contaminants dealt with included benzene, toluene, and xylene in concentration of 15 -30 ppm located 20 to 50 feet deep in a sedimentary environment. The purpose of the biological treatment was to stimulate indigenous microorganisms of the genera *Pseudomonas* and *Arthrobacter*. This was accomplished by mixing nutrients and oxygen in aqueous solution while controlling movement by pumping. The results were deemed excellent after one to three years. Oxygen dispersion rates were listed as a problem.

Chemical in situ treatment was used in the control of an acid mine drainage problem. Acid mine drainage is a major environmental problem in the coal fields in the east. These coal field spoils are characterized by high concentrations of salts and high acidity. Both originate from sulfur-bearing minerals, chiefly pyrites and marcasites.

The two primary chemical reactions are:



Further reaction of iron sulfate and sulfuric acid with surrounding rocks brings into solution other metallic elements including Ca, Mg, Al, Na, Mn, and K.

Limestone, quick lime, hydrated lime, caustic soda and soda ash are different alkalis frequently used in the treatment of acid mine drainage. Calcium compounds are much less expensive than the sodium compounds, but they react in water very slowly, cause greater hardness and produce more sludge. Precipitation of gypsum may occur where sulfates exceed 2000 mg/l. The hydroxide neutralizing compounds increase pH more substantially than carbonate compounds which influences the capability of precipitating metals such as iron and manganese. Because ferric iron will precipitate to solid ferrous hydroxide at pH 5.5 or greater and ferrous iron will convert to solid ferrous hydroxide at pH 5.0 to 9.5, hydroxide compounds are not required. Manganese, however, precipitates out as manganese hydroxide at pH 10.0 necessitating a hydroxide neutralizing agent.

Thiobacillus ferro-oxidans has been shown to be of significance in determining both the rate of initial acidification of pyrite to acid mine drainage and the level of acidity generated. These bacteria fix reduced inorganic iron and sulfur compounds and fix CO₂ to the oxidation level of a carbohydrate. One class of inhibitors, anionic detergents, has been found to be both inexpensive and environmentally safe at low concentrations. In addition, they are bactericidal only at low pH.

Other waste problems amenable to chemical treatment may involve more sophisticated treatment technology. Wuslich (1982) gives a good account of chemical treatment used on complex waste materials. Ferro-lime treatment is generally required for waters with relatively large

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concentrations of organics and metals. Iron is added either as ferric chloride or dissolved ferrous sulfate crystals. PH goes to two to act as a filter aid and reducing agent. Next, pH is raised to 11 or 12 through addition of caustic soda or some other alkaline treatment to form insoluble metal hydroxides. Oxidizing agents such as chlorine, hypochlorite or hydrogen peroxide may then be used to attack organic constituents. After this, the heavy metal hydroxide slurry is dewatered and the cake disposed of in a chemical secure landfill. Secondary treatment of the residual liquid requires pH neutralization, biological treatment or activated carbon to remove organics especially halogenated compounds, pesticides and herbicides. Hexavalent chrome must be reduced to trivalent using sodium metabisulfite. Other chemical treatments are listed below:

<u>Pollution</u>	<u>Solution</u>	<u>Chemical</u>
suspended solids	coagulation	alum
cyanides	pH adjustment oxidation	caustic soda/soda ash chlorine or sodium hypochlorite
Cr ⁺⁶	pH adjustment reduction Cr ⁺³ precipitation	sulfuric acid sodium metabisulfite caustic soda/soda ash
trace & heavy metals	precipitation flocculation	caustic soda/soda ash alum
alkaline wastes	neutralization	sulfuric acid
acid wastes	neutralization	caustic soda/soda ash
sulfate	neutralization	soda ash
fine sludge	dewater	ponding

The combination of pumping, treatment and recharge is another method of groundwater restoration being used today. In the NWWA survey, this method was most frequently used for recovery of spilled gasoline and other petroleum products. Other uses included cleaning up copper mine tailings ponds, tailings pond seepage from low and high pH

uranium tailings, precipitation of barium and removal of coliform bacteria.

Aspects to consider in the design of wells for hydrocarbon recovery include screen length and slot size. Screen length will be of longer vertical dimension to allow for the entry of floating hydrocarbons. If the screened zone is placed too deep and drawdown is not sufficient to depress the water surface to the screened zone, free floating hydrocarbons may not enter the well. Continuous slot wire-wrap screen is recommended so that the percentage of open area can be maximized. It has been demonstrated that hydrocarbons provide a good medium for bacterial growth and thus clogging of screens is generally accelerated.

Recharge systems use effluent to recharge the aquifer in order to flush contaminants and/or to control hydraulic gradients. Effluent can be discharged either downgradient or upgradient of the contamination zone. If discharged downgradient, contaminant concentration must have been reduced to allowable limits. Where the treatment does not reduce contaminants to acceptable limits in the first volume exchange, a closed loop recovery system can be installed. Effluent is then discharged upgradient and recycled through the recovery system.

The NWWA survey indicated that interceptor trenches are commonly used techniques in many instances of hydrocarbon loss. Small spills encountering a shallow barrier can be contained and/or recovered by excavating a trench (depths are usually limited to six to eight feet) and placing an impermeable barrier on the downgradient side of the trench. This allows water to pass underneath, but stops the migration of floating products. Skimmer systems can be then used to remove the floating product.

The following are selected cases from the NWWA survey on pumping, treatment and recharge.

Case 1

Seventy thousand gallons of gasoline were spilled over two acres of glacial outwash sands of very high permeability. Free gasoline was

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found floating on top of the water table approximately 30 feet below the surface. Recovery of the floating product was achieved by drilling two twelve inch diameter recovery wells screened five feet above to five feet below the water table. These were placed 135 feet apart downgradient of the plume. In addition, 30 monitoring wells were used to observe the extent of the plume and the progress of the recovery operations. The recovery wells were designed to produce a cone of depression which would capture free product and prevent further downward migration of free product. The recovery wells were pumped using submersible pumps at the rate of 300 gpm which produced a drawdown of 1.5 to 2 feet near each well. Pumping lift was about 35 feet. The extracted water was aearated during flow through a one mile long storm sewer leading to discharge into a recharge basin. The observation wells placed downgradient of the site were two-inch slotted PVC and were found to swell when in contact with gasoline.

Case 2

This case involved in situ solution mining of uranium in a sandstone unit. The specific contaminants dealt with included ammonium and other radioactive contaminants some 200 to 250 feet below the surface. Uranium milling operations tend to concentrate radioactive uranium daughter products such as ^{230}Th (half-life of 80,000 years) and ^{226}Ra (half-life of 1,620 years). Radium 226 disintegrates to form radon gas which poses a serious environmental health hazard. The USEPA requires radon flux be minimized to $2\text{pCi}/\text{m}^2\text{sec}$ by compaction over the wastes with clay or gelatinous soil/gravel mixes.

In this case, eleven existing wells in a five-spot pattern were located within the plume. The water was pumped continuously with a

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submersible pump at the rate of 30 gpm total for all wells. The water was then treated by reverse osmosis.

Case 3

High concentrations (3-5 ppm) of barium were found in groundwater. The barium was believed to originate from a natural source as barium sulfate and was being reduced to more soluble form by sulfate reducing bacteria. Chlorine was used to destroy the bacteria so that the barium would precipitate out in the limestone formation.

Case 4

In this case contamination originated from herbicide manufacturing. The waste salt pile contained sodium chloride, sodium sulfate and arsenic compounds. The plume was some 15 to 20 feet below the ground surface. Thirteen wells were constructed downgradient and within the plume in zones of highest contamination. Submersible pumps removed one to two gallons per minute per well and were run continuously. Wells were four to five inch diameter PVC with Johnson continuously slotted well screen three to five inches long. The interception and removal of the contaminated water was deemed very effective. The water was left to evaporate and the concentrated brine water deep well injected.

Case 5

Uranium tailings from an acid extraction process were cleaned up using withdrawal wells and pumped to a tailings pond for evaporation. The specific contaminants dealt with included sulphates, low pH, TDS and chlorine. Four existing wells were screened from 50% to 100% of the contaminated sandstone unit which was confined by an overlying shale layer. Withdrawal trenches were excavated through permeable alluvial cover overlying shale and the top two feet of the confined sandstone so that their total depth of 25 feet deep was six

feet below the piezometric surface. The objective of the pumping wells was to intercept contaminated water and to reverse the groundwater gradient. Monitoring wells of four inch diameter surrounding the pump back wells showed water quality improved downgradient.

Case 6

Extraction wells were used for contaminants emanating from a silver chemical plant because there were no low permeability barriers to flow and because the contaminants were sinking rapidly and were therefore unresponsive to recharge schemes. The specific contaminants dealt with included DBCP, sulfates and sulfolane. Six wells were constructed downgradient of the source. The geologic environment included complex riverine sediments with clay lenses and stringers of sand and gravel; average permeability was 500 gpd/ft². Extracted water was treated by activated carbon adsorption which decreased DBCP from about 2500 ppb to undetectable limits. Sulfates and sulfolane were not affected by treatment and water was therefore injected into an underlying aquifer 300 feet deeper than the contaminated aquifer. Total depth of the injection well was 500 feet.

With the exception of a copper mine tailings pond, very few recharge basins were apparently being tried by the industry. Recharge basins are often costly because of the time required for infiltration to occur. Recharge wells were also rarely employed. For the most part, pumping and treatment were followed by waters being discharged to streams after the operator had obtained the appropriate permit.

From this paper, it should be possible to see a wide variety of techniques are currently being used by the industry to contain and treat contamination plumes. The amounts and kinds of contaminants as well as the geologic environment where they are found will vary significantly from site to site. Evaluation and planning are

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therefore essential to a successful remedial action. This paper has attempted only to give an overview of methods currently being used in aquifer restoration and has not attempted to give a complete action agenda.

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